# Graphene quantum dots as selective fluorescence sensor for the detection of L-ascorbic acid and acid phosphatase in biological fluid via Cr(VI)/Cr(III)-modulated redox reaction

Fanping Shi,[a] Yu Zhang,[a] Weidan Na,[a] Xinyang Zhang,[b] Yan Li [a] and Xingguang Su*[a]

[a] Department of Analytical Chemistry, College of Chemistry, Jilin University, Changchun, 130012, China.

*E-mail address: suxg@jlu.edu.cn Tel.: +86 431 85168352

[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China.

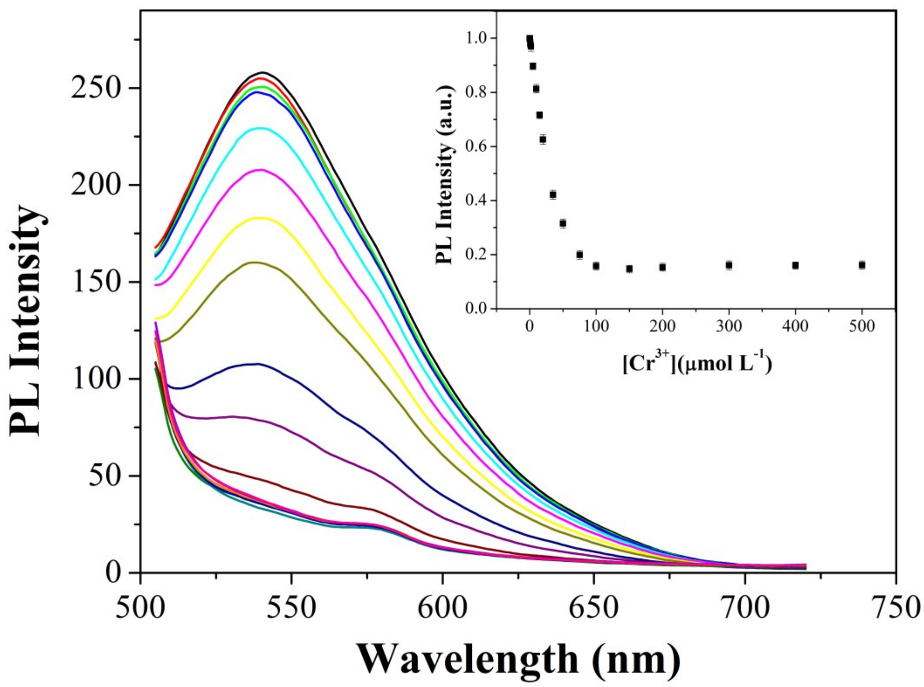


**Fig.S1** Fluorescence spectra of the GQDs in the presence of different concentrations of $Cr^{3+}$. The concentrations of $Cr^{3+}$ were 0, 0.5, 1, 2, 5, 10, 15, 20, 35, 50, 75, 100, 150, 200,300,400 and 500 mol $L^{-1}$, respectively. Inset: Plot of PL intensity of GQDs versus the concentration of $Cr^{3+}$(from 0 to 500 mol $L^{-1)}$. Tris-HCl buffer solution (10 mmol $L^{-1}$, pH 6.2) incubation for 10 minutes.

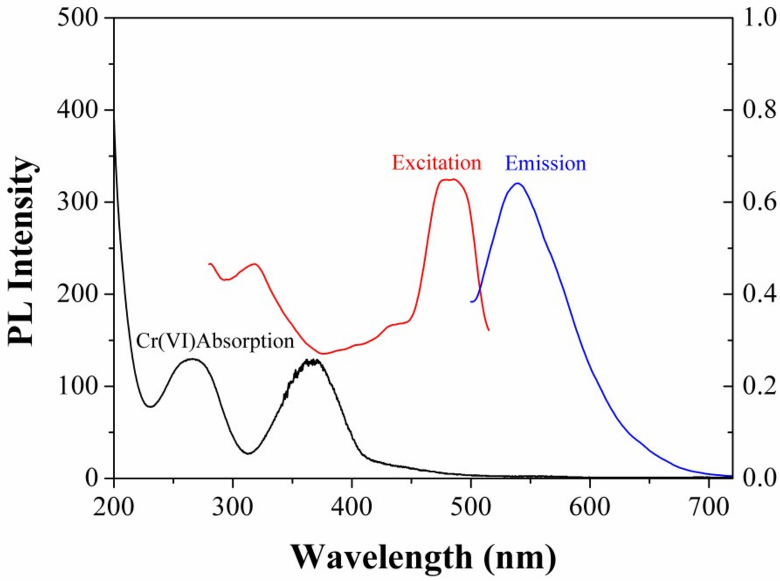


**Fig.S2** PL excitation and emission spectra of the GQDs and UV-Vis absorption of Cr(VI).

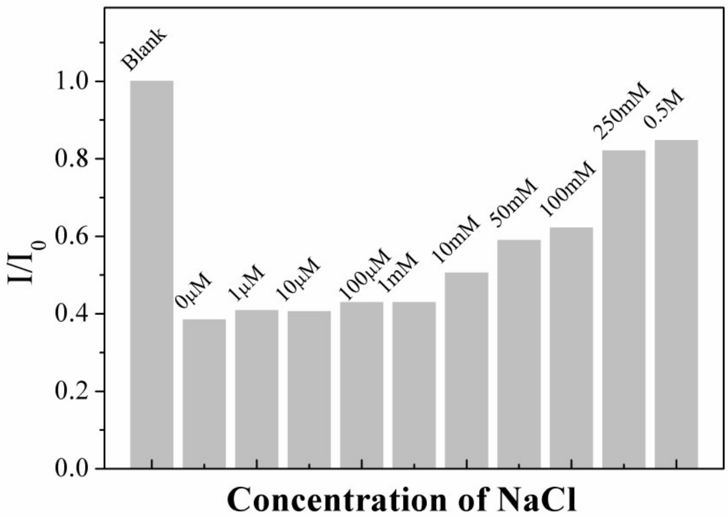


**Fig.S3** The influence of ionic strength on the quenching performance of AA to Cr(VI)-GQDs system.

**Table S1. Comparison of reported fluorescent methods for AA detection with the present method**

| Sensing system | Linear range ($\mu mol\ mL^{-1}$) | Detection limit ($\mu mol\ mL^{-1}$) | Reference |
|---|---|---|---|
| $CuInS_2$ quantum dots | 0.25-200 | 0.05 | [1] |
| Nitrogen-Doped Carbon Nanoparticles | 0.2-150 | 0.05 | [2] |
| CdTe/CdS/ZnS core/shell/shell QDs | 8-100 | 1.8 | [3] |
| Protein-modified Au nanoclusters | 1.5-10 | 0.2 | [4] |
| G-$C_3N_4$/Cr(VI) system | 0.5-200 | 0.13 | [5] |
| CQDs/AuNCs | 0.15-15 | 0.105 | [6] |
| GQDs/Cr(VI) as a redox active sensor | 0.5-250 | 0.28 | This work |

**Table S2. Comparison of performance of different methods for ACP detection**

| Type | Sensing system | Linear range (mU mL$^{-1}$) | Detection limit (mU mL$^{-1}$) | Reference |
|---|---|---|---|---|
| Colorimetric | Au-NPs incubating with NaCl | 600-7000 | 600 | 7 |
| Electrochemistry | Planar Chip Biosensors for Potentiometric Immunoassay | 0.01–4.3 | 0.01 | 8 |
| | Anionic water soluble polyfluorene derivative | 0-28nM | 4nM | 9 |
| | Cationic conjugated polyelectrolyte (PPE4+) | 0-20nM | 0.17nM | 10 |
| Fluorescence | Cationic squaraine (SQ) dyes | 0-533nM | 4.9nM | 11 |
| | Carbon Quantum Dots | 18.2-1300 | 5500 | 12 |
| | Cr(VI)-GQDs/AAP system as a redox active sensor | 0.02-3 (0.084-13nM) | 0.0089 (0.037nM) | This work |

# Reference


1. S. Liu, J. Hu and X. Su, *Analyst*, 2012, **137**, 4598-4604.
2. X. Zhu, T. Zhao, Z. Nie, Y. Liu and S. Yao, *Analytical Chemistry*, 2015, **87**, 8524-8530.
3. S. Huang, F. Zhu, Q. Xiao, W. Su, J. Sheng, C. Huang and B. Hu, *RSC Advances*, 2014, **4**, 46751-46761.
4. X. Wang, P. Wu, X. Hou and Y. Lv, *Analyst*, 2013, **138**, 229-233.
5. M. Rong, L. Lin, X. Song, Y. Wang, Y. Zhong, J. Yan, Y. Feng, X. Zeng and X. Chen, *Biosensors and Bioelectronics*, 2015, **68**, 210-217.
6. W.-J. Niu, D. Shan, R.-H. Zhu, S.-Y. Deng, S. Cosnier and X.-J. Zhang, *Carbon*, 2016, **96**, 1034-1042.
7. C. K. Tagad, S. G. Sabharwal and R. Aiyer, 2015.
8. A. H. Kamel, H. R. Galal and A. A. Hanna, *Int. J. Electrochem. Sci*, 2014, **9**, 5776-5787.
9. A. K. Dwivedi and P. K. Iyer, *Analytical Methods*, 2013, **5**, 2374.
10. Y. Xie, Y. Tan, R. Liu, R. Zhao, C. Tan and Y. Jiang, *ACS Applied Materials & Interfaces*, 2012, **4**, 3784-3787.
11. Y. Xu, B. Li, L. Xiao, J. Ouyang, S. Sun and Y. Pang, *Chem Commun (Camb)*, 2014, **50**, 8677-8680.
12. Z. Qian, L. Chai, Q. Zhou, Y. Huang, C. Tang, J. Chen and H. Feng, *Anal Chem*, 2015, **87**, 7332-7339.